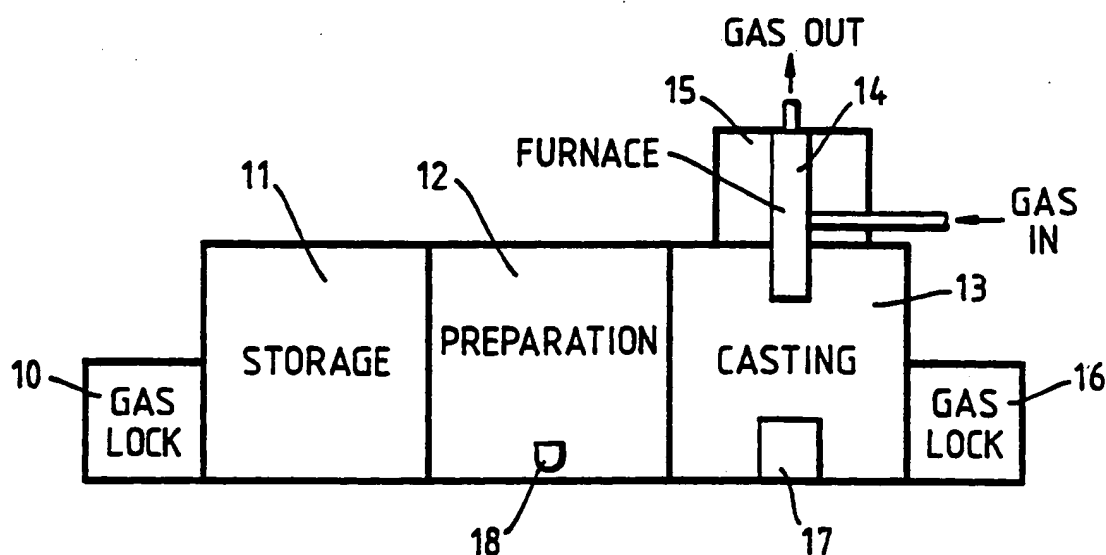




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>5</sup> : C03B 37/012, 37/023, C03C 3/32	A1	(11) International Publication Number: WO 92/00923 (43) International Publication Date: 23 January 1992 (23.01.92)
<p>(21) International Application Number: PCT/GB91/01122</p> <p>(22) International Filing Date: 9 July 1991 (09.07.91)</p> <p>(30) Priority data: 9015090.5 9 July 1990 (09.07.90) GB</p> <p>(71) Applicant (for all designated States except US): BRITISH TELECOMMUNICATIONS PUBLIC LIMITED COMPANY [GB/GB]; 81 Newgate Street, London EC1A 7AJ (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): FRANCE, Paul, William [GB/GB]; Little Cottage, Newbourne, Near Woodbridge, Suffolk IP12 4NE (GB). CARTER, Steven, Fitzgerald [GB/GB]; 62 Sherbourne Avenue, Ipswich, Suffolk IP4 3DS (GB). WILLIAMS, John, Richard [GB/GB]; 9 Denton Close, Ipswich, Suffolk IP2 9PN (GB).</p>	<p>(74) Agent: LENG, Francis, Edward; British Telecom, Intellectual Property Department, 151 Gower Street, London WC1E 6BA (GB).</p> <p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.</p> <p>Published With international search report.</p>	

(54) Title: METHOD FOR THE PREPARATION OF HALIDE GLASS ARTICLES



## (57) Abstract

Halide glass articles, e.g. rods, tubes and preforms for making fluoride glass fibres, are prepared by melting and/or casting the articles under a low pressure, e.g. 0.01 to 500 mbars and, during the low pressure regime, a gas flow rate of between 0.01 to 100 litres/min (measured at NTP) is maintained. It has been found that subjecting the melts to a low pressure reduces the attenuation of the fibre which eventually results from the melts.

Best Available Copy

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

METHOD FOR THE PREPARATION OF HALIDE GLASS ARTICLES

This invention relates to a method for the preparation of halide, preferably fluoride, glass articles, eg preforms suitable for drawing into fibre.

Halide, and especially fluoride, glass fibre is used  
5 where transmission in the wavelength band 2000nm to 4500nm is required. Halide fibres also display good transmission outside this band, eg over the range 500nm to 2000nm but competitors, eg  $\text{SiO}_2$  based fibres, have good transmission in this region. However, the  
10 competitors have such high attenuations in the band 2000nm to 4500nm that they are excluded for consideration when it is required to use the fibre at this wavelength.

In most cases, the preparation of halide fibres involves first the preparation of the core and clad  
15 glasses, the casting of these two glasses to make a preform and the drawing of the preform into fibre. It is important to avoid contamination during the preparation of the glasses and their casting. For this reason it is usual to carry out these stages in isolation chambers  
20 which are provided with a dry inert atmosphere at slightly above the pressure outside the isolation chamber. The inert atmosphere is usually nitrogen for reason of cheapness but other inert gases, eg argon or helium, could also be used. It is also advantageous to  
25 submit the melt to an oxidation process and mixtures of

inert gas and oxygen are used for this purpose. The transmission properties of a halide fibre are determined to a large extent by chemical considerations, eg the chemical composition of the core glass and the clad glass. It is also important that the two glass compositions cooperate to provide guidance and are compatible with one another during the preparative stages, especially the drawing.

The selection of the chemical compositions of the core and clad glasses together with the careful preparative techniques indicated above are important to achieve low attenuation but it appears that mechanical imperfections, eg crystals and bubbles, in the fibre can also cause attenuation, probably because mechanical imperfections can scatter the light.

This invention is based upon the discovery that mechanical imperfections can be caused during the preparation of the glasses and in the casting of the preform and it has most surprisingly been discovered that subjecting the melts to treatment under the atmospheric conditions specified below, substantially reduces the incidence of mechanical faults whereby fibre with lower attenuation is achieved. It will be appreciated that subjecting solid glass to the specified treatment will have little or no effect upon its properties and it is the molten glasses which benefit from said treatment applied during the latter stages of their preparation and/or during casting. The melting of the halide glasses is carried out in contact with atmospheres, especially controlled atmospheres, which are conveniently provided in a chamber attached to an apparatus such as a glove box. The term "controlled atmosphere" includes inert

atmospheres consisting of inert gasses such as nitrogen, helium and argon. At certain stages of the process the controlled atmosphere may be pure oxygen or oxygen mixed with an inert gas. The atmospheric conditions mentioned  
5 above comprise a low pressure preferably with a flow of gas at low pressure through the atmosphere which is in contact with the melt. Said flow of gas is preferably at a flow rate of 0.1 to 100 litres/minute, 2 litres/minute as measured at NTP. These correspond to ranges of  $7 \times 10^{-6}$  to  $7 \times 10^{-3}$  moles/second and  $1.5 \times 10^{-3}$  moles/second  
10 respectively. Said low pressure is preferably below 500 mbar, especially below 100 mbar, e.g. within the range 0.01 to 150 mbars.

15 During the casting of preforms, it is desirable that the pouring of the core is carried out at a lower temperature and pressure than the pouring of the cladding, e.g. at a temperature which is at least 20°C lower, e.g. 20 - 200°C lower than the pouring of the cladding. The cladding is  
20 preferably poured at a pressure of below 500 mbars, e.g. at a temperature at which its viscosity is 0.01 to 1000 poise and under a pressure of 2 - 100 mbars. The preferred pressure for the core is 0.01 - 2 mbars. It has been observed that these conditions also give good  
25 results even without the flow rates mentioned above.

The halide glasses mentioned above comprise (and preferably consist of) mixtures of metal halides wherein at least 90 mole %, and preferably 100 mole % of the  
30 halide is fluoride. In the case where the percentage of fluoride is less than 100%, it is preferred that the balance of the halide is entirely chloride. Of the

metals which constitute the halides preferably at least 45 mole % is Zr and at least 10 mole % is Ba. It is preferred that metals in addition to Zr and Ba are also present and these are conveniently selected from Al, La, Na, Hf and Pb. The glass composition may also include dopants, e.g. rare earth metals such as Nd and/or Er to confer lasing properties on the glass. These dopants are conveniently present in the form of halides, especially fluorides.

10       The invention relates particularly to the preparation of halide (as defined above) fibres, and especially fibres which are produced by drawing preforms with a core/cladding structure. The preforms may be made by casting a tube of a first halide glass, and, before 15 the tube cools, casting a second halide glass into its bore. Alternatively, a preform may be assembled by casting tubes and rods, and shrinking the tubes onto the rods.

20       In addition tubes may be shrunk onto preforms as described above. This is convenient for making preforms with more than 2 regions, e.g. using more than 2 different glass compositions and for making preforms with large cross sectional areas. It is also convenient to shrink tubes onto preforms when it is desired to make 25 fibre with small cores. This usually implies a fibre in which the cross-sectional area of the cladding is large in relation to the cross-sectional area of the core. The conventional method, in which the core is cast into a tube of cladding, is mechanically difficult because of 30 the small diameter of the tube. This difficulty can be avoided by casting a preform in which the size of the

core precursor is convenient for casting. Stretching the preform so that its diameter is reduced about 2 - 20 times, reduces the size of the core but the preform no longer has an adequate diameter. Therefore shrinking a tube of cladding glass onto the reduced preform restores the external dimension.

The glasses which are used for casting the articles previously identified, i.e. tubes, rods and preforms, may be prepared by melting together the appropriate fluorides or by fluorination of the appropriate oxides. These preparative methods are described in greater detail below. In addition the melts needed to cast the articles may be prepared by melting previously formed glass compositions. In any case, however the glass melt is prepared, the low pressure treatment specified above is applied either to the melt immediately before casting, or to the melt during casting, or during both stages.

The invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a diagram illustrating isolation chambers suitable for the preparation of fibre preforms;

Figure 2 is a diagrammatic illustration of a furnace suitable for melting halide glasses in accordance with the invention;

Figure 3 is an illustration of a moulding box suitable for making preforms in accordance with the invention; and

Figure 4 is attenuation curves comparing fibres prepared by different techniques.

The isolation chambers shown in Figure 1 comprise a gas lock 10 for introducing chemicals, crucibles and other equipment into the inert atmosphere. The gas lock 10 provides easy access to a storage chamber 11 in which materials and equipment can be retained until required. The storage chamber 11 gives access to a preparation chamber 12 via a hatch (not shown). Crucibles 18 can be placed in the preparation chamber and charges to make desired glass compositions are weighed into a crucible. (Where it is appropriate to distinguish, 18B will be used to denote a crucible used for cladding glass and 18A to denote a crucible used for core glass).

The preparation chamber 12 gives direct access, via a hatch (not shown), to the casting chamber 13. A furnace 14 is located vertically above the casting chamber 13. Said furnace is located in a furnace chamber 15 and its lower end extends into the casting chamber 13 for ease of access. The casting chamber 13 contains a moulding box 17 and it is provided with a gas lock 16 which is used to take fibre preforms out of the isolation chambers. The furnace 14 is shown in greater detail in Figure 2 and the moulding box 17 is shown in greater detail in Figure 3.

All the gas locks and chambers shown in Figure 1 are provided with a supply of nitrogen (not shown) and with vents to allow used nitrogen to go to waste. The chambers are permanently flushed with dry nitrogen (less than 10ppm of water) which is maintained at a pressure slightly higher than the external so as to reduce the risk of contamination entering the isolation chambers.

The isolation chambers shown in Figure 1 make it



possible for chemicals and other materials to be stored permanently in a dry atmosphere so that the risk of contamination is substantially reduced. In addition, all blending, melting and casting operations are carried out under a pure, dry atmosphere so that the risk of introducing impurities during handling is substantially reduced. Each chamber has its own separate supply for the dry atmosphere and hatches are normally closed between the chambers. Thus the risk of cross-contamination between the chambers is substantially reduced. It has been found that these precautions are necessary because even slight contamination can substantially increase the attenuation of fluoride glass fibres.

When crucibles 18 have been charged in the preparation chamber 12 (and lids applied to reduce the risk of contamination), they are transferred to the casting chamber 13 and introduced into the furnace 14. The ingredients are melted in the furnace 14 and the crucibles 18, complete with hot, molten charges are returned to the casting chamber 13. When the preforms have solidified and cooled, they are removed via the gas lock 16 for drawing to fibre.

It should be noted that crucibles are usually processed in pairs, ie one crucible 18A for the core glass and the other crucible 18B for the clad glass. More details of processing will be given below.

There are two basic processes for the preparation of fluoride glasses and the two processes will be described briefly. The isolation chambers shown in Figure 1 are suitable for both processes.

According to the first process oxides of the selected metals are weighed in the preparation chamber 12 and mixed thoroughly in a crucible. In addition to the oxide powders ammonium bifluoride,  $\text{NH}_4\text{F} \cdot \text{HF}$ , is introduced into the crucible. In the furnace 14 the ammonium bifluoride decomposes and converts the oxide to fluorides.

In the alternative process the selected fluorides are weighed and mixed in the crucible. With this process it is not always necessary to use the ammonium bifluoride because no chemical reaction is intended. However, as a precautionary measure, it is common to introduce a small amount of ammonium bifluoride into the crucible in case the fluoride powders are contaminated by oxides.

It should be realised that hydroxide and oxide are the two most obnoxious contaminants in fluoride fibres and, therefore, it is important to reduce the level of these contaminants to the minimum.

The furnace, shown as 14 in Figure 1, comprises a body 20 which includes insulation and electric heating elements. The body has an inlet port 23 situated near the bottom and a vent 24 at the top.

The inlet port 23 is connected to a nitrogen mass flow valve 25 and an oxygen mass flow valve 26. These valves are adjustable during melting operation to provide a controlled and variable atmosphere during processing. The vent 24 is connected to a controllable exhaust pump 27 so that the pressure in the furnace can be varied. In addition, the furnace is provided with a thermometer 28 for measuring the temperature of operation.

For the convenience of the operatives the system includes a microprocessor 29 which is operatively connected to:

- 5       the nitrogen mass flow valve 25,
- the oxygen mass flow valve 26,
- the exhaust pump 27,
- the thermometer 28, and
- the electric supply to the furnace.

10       The microprocessor 29 includes a timing means as well as a storage facility for storing programs to operate the furnace for production runs which programs include data defining an operational sequence. Thus the microprocessor 29 provides automatic means for performing complicated production schedules without the detailed  
15       attention of the operators. The microprocessor 29 can be programmed to emit a signal to attract the attention of operators when a production schedule has been completed.

20       During a melting schedule, the base of the furnace is closed by means of a closure plate 19 which seals the furnace to prevent the contamination of the furnace chamber 15 by gases evolved during heating. It is convenient to support the crucibles 18A and 18B by means of the closure plate 19.

25       Before a melting operation crucibles 18A and 18B, at this stage containing the precursors of the glasses in the form of mixed powders, are introduced into the furnace and the closure plate 19 is applied to seal the furnace. (If it is intended to apply identical melt schedules to both furnaces then it is convenient for both  
30       crucibles to go into the same furnace. If different melt schedules are intended it is necessary to use two furnaces.)

At this stage a supply of nitrogen, at ambient pressure, is passed through the furnace or furnaces. A typical melt schedule is as follows:

- 5 (1) In a controlled atmosphere, the crucibles 18A and 18B are raised to the temperature at which any  $\text{NH}_4\text{F} \cdot \text{HF}$  reacts. This temperature is usually in the range 200 to 500°C.
- 10 (2) The crucibles are maintained at this temperature for a period of 30 to 90 mins to allow completion of any reactions which occur. A stream of gas removes any vapours which are evolved during this stage.
- 15 (3) The temperature in the furnace is raised, eg to 700 to 900°C, to ensure that all the components have passed into solution. This stage is conveniently carried out under the ambient pressure in the isolation chambers.
- (4) The melts are oxidised for 10 to 150 minutes. Oxygen was used as the oxidising agent.
- 20 (5) When the temperature of the glass has reduced by at least 50°C the setting on the nitrogen flow valve 25 is reduced to zero whilst continuing with the flow of oxygen and the exhaust pump 27 started. This reduces the pressure in the furnace to about 50mbar. This has the effect that the last stage of the melting is carried out under reduced pressure in accordance with the invention. The atmosphere may be pure  $\text{O}_2$  at this stage. The temperature should be at least 600°C.
- 25 (6) The supply of nitrogen is re-started and the supply of oxygen is terminated. When the oxygen is clear of the furnace the closure plate 19 is removed and
- 30

the crucibles are transferred into the casting chamber 13.

The structure and use of the casting box 17 will now be described.

5       The oxygen treatment, ie step (4), is described in our patent portfolio consisting of EP 170380, US 4741752, US 4848997 and CD 1267537.

10       After removal from the furnace 14 the hot crucibles 18A and 18B, containing molten glass, are placed in the casting box 17 for the formation of the preform.

15       The casting box 17 has a lid 30 which opens to allow the entry of the crucibles 18A and 18B. When the lid 30 is closed the pressure in the box 17 can be reduced. The box 17 contains a conventional mould for the centrifugal casting of tubes. This comprises a tubular mould 31 which can be rotated about its longitudinal axes to provide the centrifugal force for casting and which can be tilted between the horizontal and the vertical. Since this is a conventional arrangement for the centrifugal casting of tubes, it will not be described in detail. 20       The box 17 also contains manipulators 32 and 33 and it also has a vent 34 for connection to suction to reduce the pressure.

25       After melting in the furnace, the hot crucibles 18A and 18B are transferred into the holders 32 and 33 and the lid 30 is closed. At this stage suction can be applied to the vent 34 so that the pressure in the box 17 is reduced. Preferably the box 17 is not completely sealed since it is desired to cause a constant flow of 30       nitrogen through the box during the casting process. Suitable flow rates are 0.01 to 100 litres/min,

preferably 0.1 to 10 litres/min, (as measured at NTP).  
The pressure in the box and the temperature of the glass  
vary during the casting process. These variations will  
be briefly described.

5

Initially the pressure is reduced below 500 mbars  
preferably to a pressure of 2 - 100 mbars. Under a  
pressure within this range the manipulator 33 is used to  
pour the cladding glass into the mould 31 and, when it is  
10 poured, the viscosity of the cladding glass is preferably  
0.1 to 1000 poise. (This often requires a temperature in  
the range 450 - 600°C for lasers with more than 50 mole %  
ZrF<sub>4</sub>). After pouring, the mould is rotated about its  
longitudinal axis and this causes the molten glass to be  
15 distributed evenly around the mould 31 so that a tube is  
formed. At this stage the temperature must be high  
enough so that the glass is sufficiently mobile to form a  
good tube but the high temperature makes it desirable to  
maintain the pressure above a minimum determined by the  
20 temperature of the glass. This avoids vapourisation of  
volatile components which could re-condense and  
contaminate the preform. Even trivial amounts of re-  
condensation can cause substantial defects by nucleating  
crystal growth. Thus at temperatures close to 600°C it  
25 would be undesirable to use pressures substantially below  
100 mbars. Because of the chilling caused by the mould  
31 the cladding glass is cooled and it solidifies. The  
core glass in the crucible 18A cools, but not as quickly  
as the cladding glass in the mould 31, so that the core  
30 glass remains mobile. When the cladding glass is  
sufficiently solidified the rotation is terminated and

the longitudinal axis of the mould is tilted back to the vertical orientation. At this point the manipulator 32 is used to pour the core glass from the crucible 18A into the bore of the tube which has just been formed. This operation is performed at a temperature which is lower than the temperature at which the cladding glass was poured, e.g. at a temperature which is 20 - 200°C lower. It will be appreciated that the lower temperature means that the core glass will have a substantially higher viscosity than the cladding glass during pouring but it has been found that this still allows good casting of the core to be achieved. At these lower temperatures, the pressure in the system can be further reduced so that the core glass is cast at a pressure below that at which the cladding glass was cast. Conveniently the core glass is cast under pressure of 0.01 to 2 mbars. The casting of the core completes the casting operation and the preform is allowed to cool under a reduced pressure.

When the preform has cooled enough to be handled, the suction at vent 34 is terminated, the pressure in the box 17 allowed to return to the ambient pressure in the casting chamber 13, and the preform is annealed in the mould. When it has cooled the mould 31, containing the solid preform, is now removed from the isolation chambers via the gas lock 16.

The preform, which has been prepared in accordance with the invention because the last stages of the melting and the casting were carried out under reduced pressure, is converted into fibre using conventional techniques. The preform may be drawn in the form in which it was cast but improved fibre performance may be obtained by the use of one or more of the following features.

### Polishing

Poor surface quality can sometimes impair the strength of fibre and increase the loss. Therefore, it may be desired to polish the surface of the preform preliminary to drawing. The polishing may be carried out mechanically using abrasives.

### Etching

Gentle chemical etching, eg using a solution of  $ZrOCl_2$ , to remove surface layers which may be contaminated. Etching is often appropriate to remove abrasives which have been used in a previous polishing stage.

### Ion bombardment

It has been found that placing the preform in a vacuum chamber and bombarding it with suitable ions can remove a very thin surface layer. This is valuable where contamination is limited to very thin surface layers and the use of a vacuum reduces the risk of recontamination.

### Protective Coating

As a final treatment before drawing, it is often convenient to apply a protective coating to the surface of the preform. Chalcogenide glasses have been recognised as a particularly suitable form of coating because they form barrier layers to protect the fluoride fibre from a hostile environment. Very thin layers of chalcogenide glass can be applied by ion beam sputtering in the same vacuum chamber which is used for bombardment. This allows at least a preliminary coating to be applied to the preform while it is still under vacuum and before exposure to the air allows recontamination.



(One form of ion bombardment and coating are described in our patents EP 266889 and US 4863237).

Finally, using conventional techniques, the preform is drawn so that its diameter is reduced in the ratio (20 - 220): 1, e.g. 80:1, so as to produce the fibre which is the ultimate product of the invention. It has been demonstrated that the use of low pressures as described above can reduce the attenuation of the fibre by a factor of about 10. It can also improve the mechanical strength of the resulting fibres.

Three fluoride glass fibres were prepared by three different methods. Each of the fibres had the composition specified in the following table.

	<u>Component</u>	<u>Core Glass</u>	<u>Cladding Glass</u>
15	ZrF <sub>4</sub>	58.6	62.1
	BaF <sub>2</sub>	23.2	24.6
	LaF <sub>3</sub>	7.1	5.6
	AlF <sub>3</sub>	1.9	1.8
	NaF	5.1	5.9
20	PbF <sub>2</sub>	4.1	0

wherein the numbers represent percentage by weight.

A more detailed description of these fibres is given in our patents EP 170380 and US 4836643.

Fibre A was prepared by the preferred embodiment of the invention using a low pressure treatment during both melting and casting.

Fibre B was also prepared according to the invention but using the low pressure treatment during melting only.

Fibre X was prepared according to the prior art without any low pressure treatment.

Figure 4 shows the attenuation for all three fibres and it is easy to see that the low pressure treatment according to the invention substantially reduces the attenuation.

5       The minimum attenuation is at about 2700nm in each case and the attenuations are:

Fibre A	1.5dB/km
Fibre B	6.5dB/km
Fibre X	20.5dB/km.

10

CLAIMS

1. Method of preparation of halide glass articles which method comprises treating melts of said halide glass  
5 under a flow of gas at low pressure during the preparation of the melts or during the casting of said melts or during both said preparation and said casting wherein at least 90 mole % of the halide of said halide glass is fluoride and said article is selected from rods,  
10 tubes and fibre preforms which preforms include a core precursor and a cladding precursor.
2. A method according to claim 1, wherein the low pressure is within the range 0.01 to 500 mbars.
3. A method according to claim 2, wherein the low  
15 pressure is within the range 0.1 to 100 mbars.
4. A method according to any one of claims 1, 2 or 3, wherein the flow of gas is maintained at a gas flow rate of between 0.01 to 100 litres/min as measured at NTP.
5. A method according to claim 4, wherein the flow rate  
20 is between 0.1 and 10 litres/min.
6. A method according to any one of the preceding claims, wherein the gas present during the low pressure melting treatment includes oxygen.
7. A method according to any one of the preceding  
25 claims, wherein the low pressure casting treatment is carried out under a dry inert atmosphere.
8. A method according to any one of the preceding claims, wherein the treatment of the melt comprises:
  - (a) A preliminary melting phase which is conducted in  
30 the presence of a dry atmosphere at ambient pressure;
  - (b) An oxidation phase in which the melted glass is contacted at ambient pressure with a dry atmosphere being either oxygen or a mixture of oxygen and inert

gas, said atmosphere containing oxygen and inert gas  
in the mole ratio  $O_2$ :inert gas = 1:0 to 1:100.

9. A method according to any one of the preceding  
claims, wherein all of the halide of said halide glass is  
fluoride.

10. A method according to claim 9, wherein the fluoride  
glass consists essentially of at least one fluoride  
selected from fluorides of Zr, Ba and Al together with at  
least one fluoride selected from fluorides of Na, Al, La,  
Pb and Hf.

11. A method according to any one of the preceding  
claims, wherein the article is a preform for drawing into  
fibre, said preform comprising a core of one halide glass  
and a cladding of a different halide glass and wherein  
each of the two glasses is prepared and/or cast under the  
conditions specified in any one of the preceding claims.

12. A method of preparing a halide glass fibre, which  
method comprises preparing a preform by a method  
according to claim 11 and thereafter drawing said preform  
into fibre.

13. A method of preparing a fluoride glass fibre which  
fibre comprises a core of a second fluoride glass  
surrounded by and in contact with a cladding of a first  
fluoride glass wherein the refractive index of the second  
fluoride glass is higher than the refractive index of the  
first fluoride glass, which method comprises:

- (a) providing the precursors of said first fluoride  
glass into a first crucible,
- (b) providing the precursors of said second  
fluoride glass into a second crucible,
- (c) transferring both of said crucibles into the  
same furnace or different furnaces and  
subjecting both crucibles simultaneously to a

melting regime comprising, in the order specified,

(c1) pre-heating said crucibles in the presence of a dry gas at ambient pressure until any evolution of gas has ceased,

(c2) heating said crucibles at a temperature above the melting point of the glasses in the presence of a mixture of oxygen and inert gas in the mole ratio 1:0 to 1:100,

(c3) reducing the pressure in the furnace to below 500 mbars and maintaining a gas flow 0.01 to 100 litres/min (as measured at NTP) whereby the melts are treated under a low pressure regime,

(d) transferring the crucibles to a casting zone and casting said first glass composition as a tube and casting said second glass composition into the bore of said tube whereby a fibre preform is produced, both of said castings being conducted under a pressure of less than 150 mbars and a flow rate of 0.01 to 100 litres/min (as measured at NTP), and

(e) drawing the fibre preform into a fibre.

14. A method of preparing a halide glass fibre which method comprises preparing a preform which includes a core precursor and a cladding precursor and drawing said preform into fibre, wherein said preform is prepared by casting said cladding precursor as a tube and thereafter casting said core precursor into the bore of said tube, characterised in that the cladding precursor is poured into a mould under reduced pressure, and the core precursor is poured into said bore under a pressure which is lower than the pressure at which the cladding

precursor was poured and at a temperature which is lower than the temperature at which the cladding precursor was poured.

5 15. A method according to claim 14 in which the cladding precursor is poured at a pressure below 150 mbars.

16. A method according to either claim 14 or claim 15, in which the core precursor is poured at a temperature which is 20 - 200°C lower than the temperature at which the cladding precursor was poured.

10 17. A method according to claim 16, wherein the cladding precursor is poured at a temperature at which its viscosity is 0.01 to 1000 poise and under a pressure of 2 - 100 mbars.

15 18. A method according to either claim 16 or claim 17, wherein the core precursor is poured under a pressure of 0.01 to 2 mbars.

19. A method according to any one of claims 14 - 18, wherein all of the halide of said halide glass is fluoride.

20 20. A method of preparing a fluoride glass fibre which fibre comprises a core of a second fluoride glass surrounded by and in contact with a cladding of a first fluoride glass wherein the refractive index of the second fluoride glass is higher than the refractive index of the first fluoride glass, which method comprises:

- 25 (a) providing the precursors of said first fluoride glass into a first crucible,
- (b) providing the precursors of said second fluoride glass into a second crucible,
- 30 (c) transferring both of said crucibles into the same furnace or different furnaces and subjecting both crucibles simultaneously to a

melting regime comprising, in the order specified,

- 5 (c1) pre-heating said crucibles in the presence of a dry gas at ambient pressure until any evolution of gas has ceased,
- (c2) heating said crucibles at a temperature above the melting point of the glasses in the presence of a mixture of oxygen and inert gas in the mole ratio 1:0 to 1:100,
- 10 (c3) reducing the temperature in the furnace to by at least 50°C but not to a temperature below 600°C and applying a pressure in the range 5 - 150 mbars,
- (d) transferring the crucibles to a casting zone and,
- 15 (d1) casting said first glass composition as a tube wherein said casting includes pouring said first glass composition into a mould at a temperature at which its viscosity is 0.01 to 1000 poise under a pressure of 2 - 100 mbars,
- 20 (d2) casting said second glass composition into the bore of said tube whereby a fibre preform is produced, wherein the pouring of said first glass composition into said bore is carried out at a temperature which is at least 20°C lower than the temperature used in step (d1) and under a pressure in the range 0.01 - 2 mbars, and,
- 25 (e) drawing the fibre preform into a fibre.

1/2

Fig. 1.

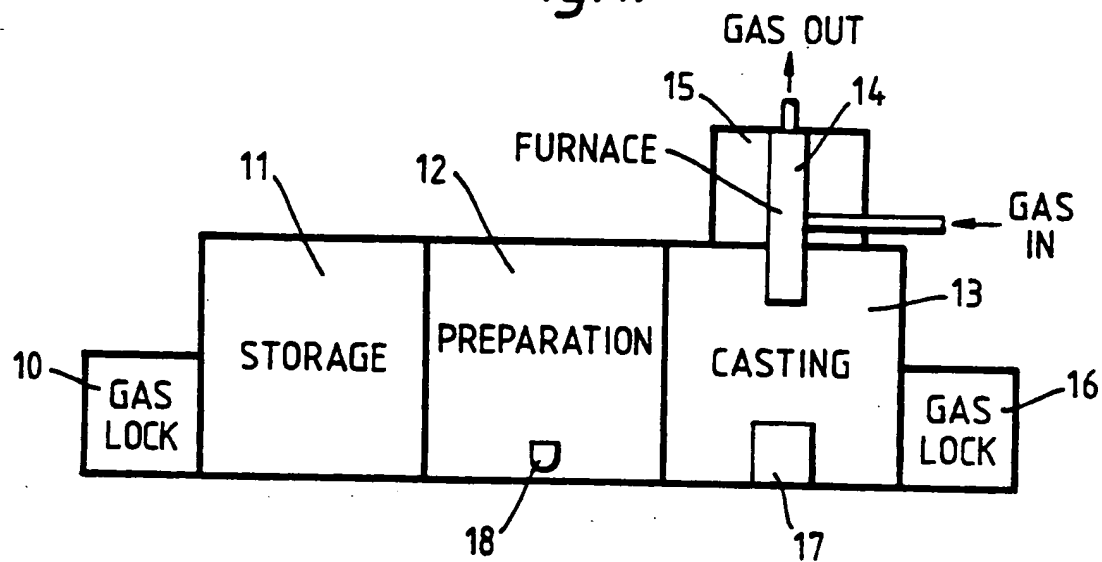
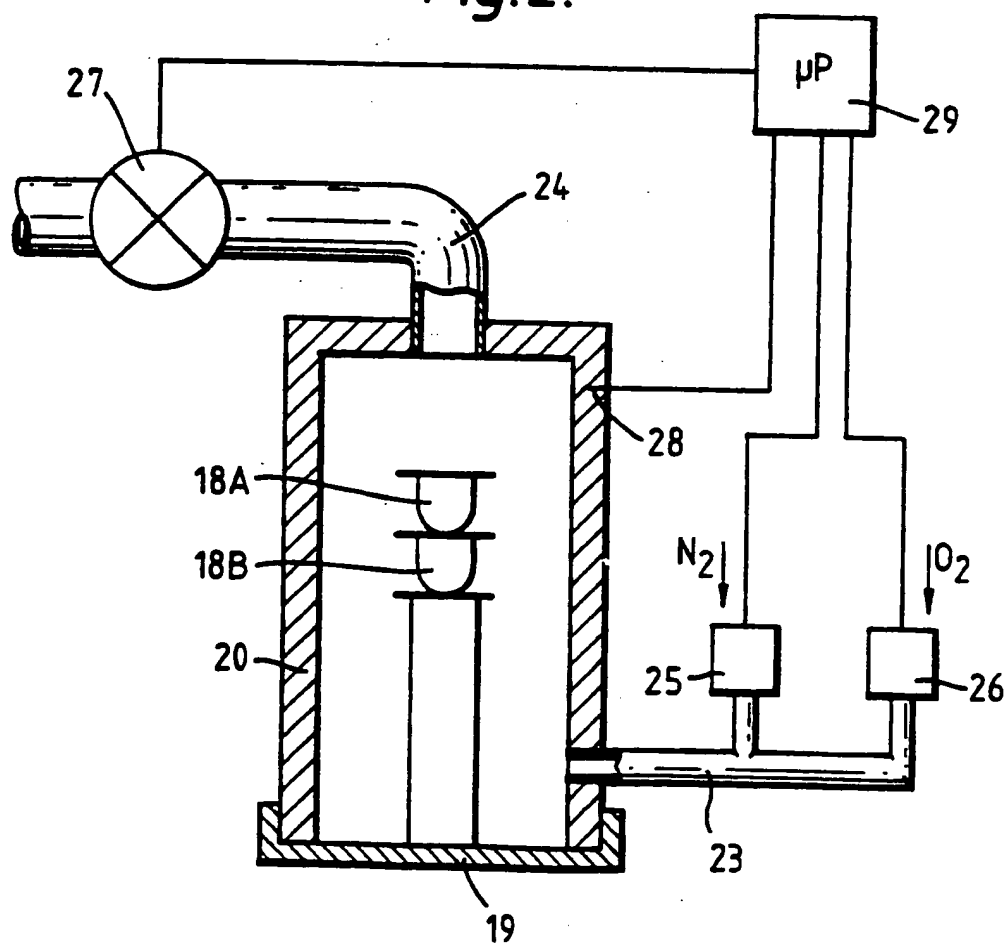


Fig. 2.





2/2

Fig.3.

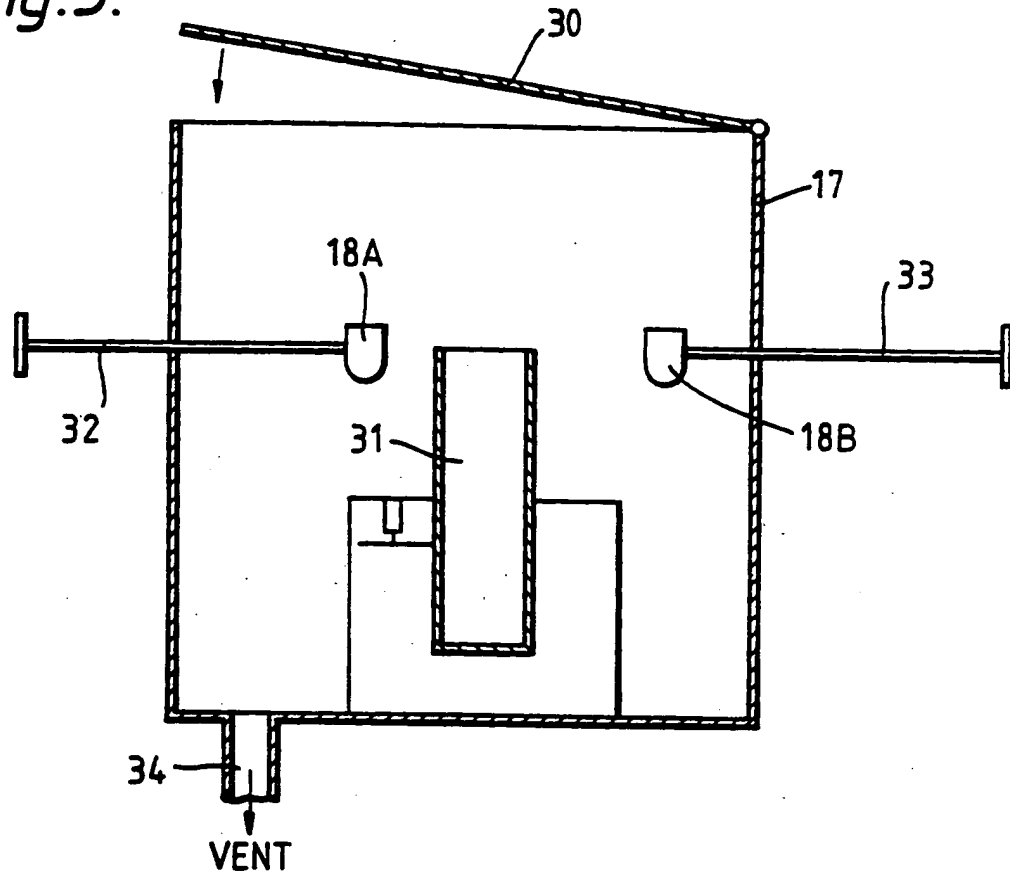
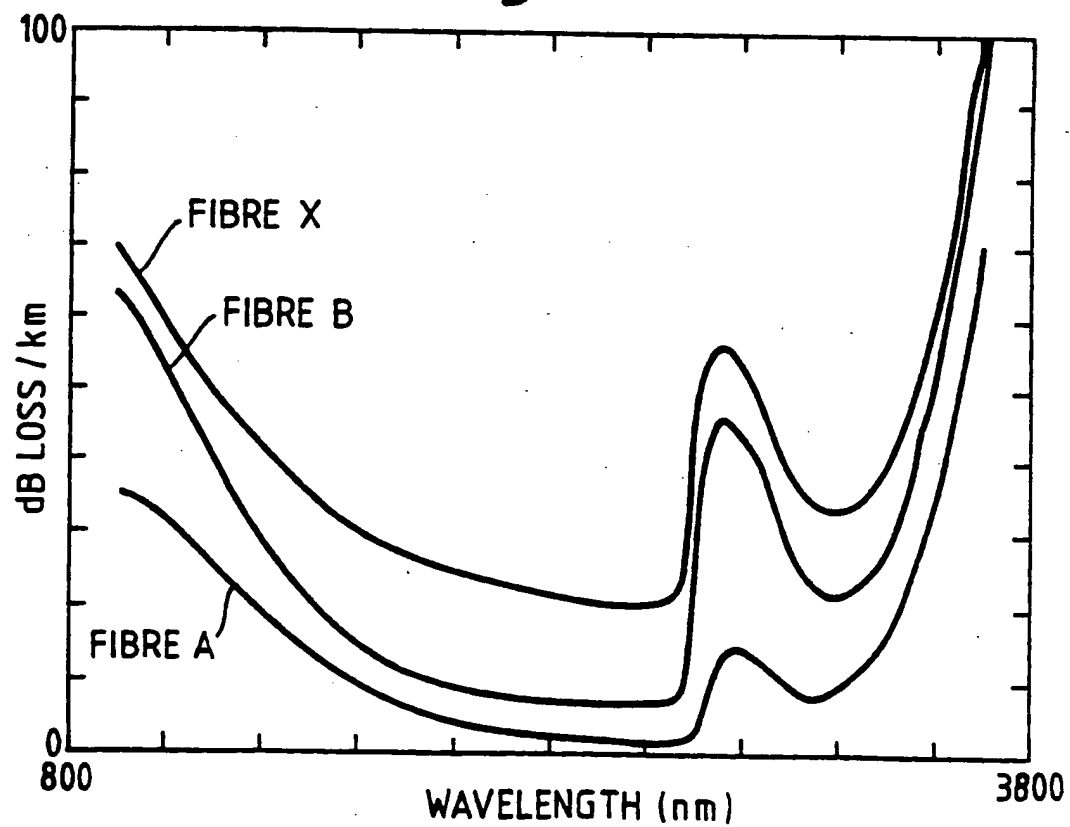


Fig.4.



# INTERNATIONAL SEARCH REPORT

International Application

PCT/GB 91/01122

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl. 5      C 03 B 37/012      C 03 B 37/023      C 03 C 3/32

## II. FIELDS SEARCHED

### Minimum Documentation Searched<sup>7</sup>

Classification System

Classification Symbols

Int. Cl. 5      C 03 B      C 03 C

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP, A, 0161999 (LE VERRE FLUORE S.A.) 21 November 1985, see claims 1-7, 12; example 4; page 8, lines 23-30; page 10, lines 5-8	1
A	---	6, 7, 9-13, 20
X	US, A, 4897100 (M. L. RICE) 30 January 1990, see claims 10, 17, 18; figure 2; column 4, lines 14-23	1
A	---	6-14, 20
A	Patent Abstracts of Japan, vol. 12, no. 410 (C-540)[3257], 28 October 1988, & JP, A, 63147838 (NIPPON TELEGR. & TELEPH. CORP.) 20 June 1988 --- -/-	1

<sup>10</sup> Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

26-09-1991

Date of Mailing of this International Search Report

29. 10. 91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

*[Signature]* TORIBIO

## III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	Patent Abstracts of Japan, vol. 14, no. 184 (C-709)[4127], 13 April 1990, & JP, A, 2030635 (SUMITOMO ELECTRIC IND. LTD) 1 February 1990 ---	1
A	EP,A,0336280 (GTE LABORATORIES INC.) 11 October 1989, see claim 2; page 4, lines 21-55 ---	1,7,9, 10
A	WO,A,8607587 (HUGHES AIRCRAFT CO.) 31 December 1986, see claims 1,4,9; page 8, line 6 - page 9, line 17 ---	1,4-10
A	EP,A,0170380 (BRITISH TELECOM PLC) 5 February 1986, see claims; examples 1,5 (cited in the application) ---	1,4-13, 20
A	US,A,4885019 (J.J. HUTTA) 5 December 1989, see claims; column 2, lines 52-54; column 6, lines 11-19 ---	1,9-12
A	Chemical Abstracts, vol. 102, no. 24, 1985, (Columbus, Ohio, US), see pages 280-281, abstract 208282a, & JP, A, 6011239 (NIPPON TELEGRAPH AND TELEPHONE PUBLIC CORP.) 21 January 1985 -----	1-3

# ANNEX 1 THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

GB 9101122

SA 49440

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/10/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0161999	21-11-85	FR-A- 2563826	08-11-85
		AU-B- 584335	25-05-89
		AU-A- 4206085	14-11-85
		CA-A- 1261631	26-09-89
		JP-A- 60246240	05-12-85
		US-A- 4659355	21-04-87
US-A- 4897100	30-01-90	None	
EP-A- 0336280	11-10-89	AU-A- 3116689	05-10-89
		JP-A- 1290541	22-11-89
		US-A- 4946490	07-08-90
		US-A- 5015281	14-05-91
WO-A- 8607587	31-12-86	US-A- 4659352	21-04-87
		EP-A, B 0227792	08-07-87
		JP-T- 62502042	13-08-87
EP-A- 0170380	05-02-86	CA-A- 1267537	10-04-90
		JP-A- 61101423	20-05-86
		US-A- 4848997	18-07-89
US-A- 4885019	05-12-89	None	

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**